between the two have narrowed significantly. Improving fundamental understanding of the flotation process remains the main focus of research for the future. The areas where significant advances are anticipated include: (i) design and synthesis of more effective, environmentally friendly flotation reagents (mainly collectors, frothers and depressants); (ii) engineering of a pulp potential monitor (mineral electrodes) and control in sulfide flotation practice; (iii) development of new flotation cells to maximize separation efficiency and minimize energy consumption; (iv) understanding and utilization of biotreatment to replace both collectors and depressants; and (v) design of a better and reliable process control system based on further development of sensors and simulators. The main challenge that flotation engineers and scientists are facing is to develop viable process alternatives for fine particle flotation. Four areas of immediate interests are: (i) the development and understanding of high intensity conditioning ; (ii) hydrodynamic cavitation in flotation machines; (iii) selective aggregation by coagulation, flocculation or oil agglomeration; and (iv) practical conditions for collectorless flotation of sulfide ores.

Further research is needed in the area of flotation chemistry and implementation of the outcome into process development. All of these are driven by the depletion of rich and simple mineral resources, reduction of metal prices and the increase of environmental pressures. The processing of tailings with a gravity concentrator at Laurium, from 1864 to 1920, left tailings containing 3% lead, these were reprocessed again in 1955 by flotation with a resulting tailings assay of 0.3% lead. It is not unrealistic to suggest that the resultant tailings may be reprocessed in the future with further innovative developments, such as integration of biotreatment in flotation. To conclude, there is a long-awaited need to widen the range of flotation applications to nonmineral-processing applications, such as in material recycling and waste remediation, with revolutionary changes in flotation technology.

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DropBooks

Hydrophobic Surface State Flotation

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Introduction

The essence of particle separation by flotation is the creation of a hydrophobic surface state, i.e. a surface that is not wetted by water, a particle surface at which bubble attachment will occur leading to flotation due to the buoyancy of the particle–bubble aggregate. (Particle flotation can also, however, be accomplished by bubble entrapment rather than by bubble attachment. For example, entrapment of air during particle aggregation/flocculation can lead to the flotation of aeroflocs.) In many instances this hydrophobicity must be established in a selective manner, frequently by collector (surfactant) addition, so that one particle type can be separated from other particle types which are maintained in a hydrophilic state.

The extent to which a surface is hydrophobic can be described in various ways. Two of the most common laboratory methods are contact-angle measurement and bubble attachment time measurement. The contact angle measurement tends to be an equilibrium, or pseudo-equilibrium, measure of hydrophobicity, while the bubble attachment time measurement is a kinetic measure of hydrophobicity. Other measures of hydrophobicity are also possible and include bubble pick-up and microflotation experiments.

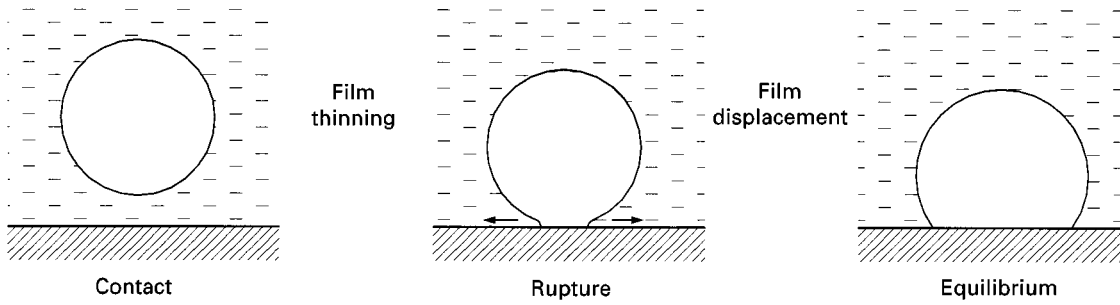

Figure 1 Bubble attachment. Sequence of events.

Bubble Attachment

Bubble attachment at a hydrophobic surface occurs due to the instability of the aqueous film that separates the bubble from the surface. As the bubble approaches the surface, to such a separation distance that the bubble may be distorted, there is a thinning of the aqueous film to the point at which rupture occurs. This time of film thinning is called the 'induction time'. After rupture, the film is displaced as it recedes across the hydrophobic surface to establish the equilibrium contact angle. The total time of film thinning and film displacement is the bubble attachment time. The sequence of events at a polished surface is depicted in **Figure 1**, where the bubble attachment time is shown to consist of the film thinning (induction) time and the film displacement time. Thus the bubble attachment time is, in part, a measure of hydrophobicity and can vary from less than a millisecond to several seconds in magnitude. Although the hydrophobicity should be an intrinsic property of the system, the bubble attachment time measurement is significantly influenced by the experimental method. For example, the bubble attachment time for a sample of naturally hydrophobic bituminous coal was found to vary by a factor of more than 50 when the results obtained for a polished surface are compared with those obtained for a particle bed as revealed in **Table 1**. Similar results have been reported for chalcopyrite. The very strong effect of contact area, hydrodynamics, and surface morphology are revealed from these data. For a given experimental teachique, the shorter the bubble attachment time, the greater the hydrophobicity.

Table 1 Measured bubble attachment times for a low-volatile bituminous coal at a polished surface and at a bed of particles (100 × 200 mesh)

Mode of attachment	*Gas phase*	*Attachment time (ms)*
Polished surface	Air	180–200
	N_2	170–190
	CO_2	140–150
Particle bed	Air	3
	N_2	–
	CO_2	3

Contact Angle

The equilibrium state for the attached bubble is described by the contact angle, θ, as indicated in **Figure 2**. The contact angle for this three-phase equilibrium is related to the respective interfacial tensions by Young's equation,

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta$$

The attachment process should be spontaneous for all finite contact angles, but generally a contact angle of at least 20° is required for bubble attachment and flotation. The greater the contact angle, the greater the hydrophobicity. Of course contact angles much greater than 20° are desired in order to make effective flotation separations. Generally the characteristic contact angles for flotation systems rarely exceed 100°. Typical values for naturally hydrophobic minerals are given in **Table 2**. Larger contact angles are

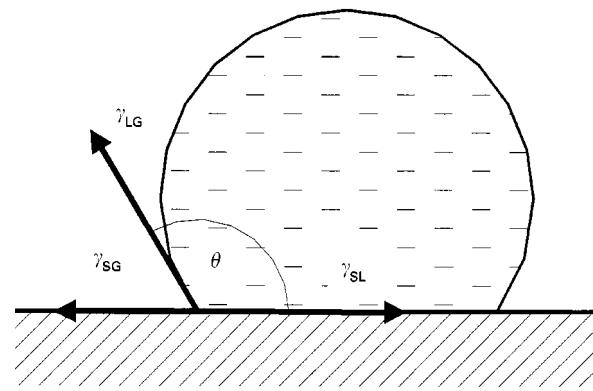

Figure 2 Equilibrium state for water drop at a hydrophobic surface.

Table 2 Naturally hydrophobic minerals and respective contact angles

Mineral	*Composition*	*Surface plane*	*Contact angle (degrees)*
Graphite	C	0001	86
Coal	Complex hydrocarbon		20–60
Sulfur	S		85
Molybdenite	MoS_2	0001	75
Stibnite	Sb_2S_3	010	
Pyrophyllite	$Al_2(Si_4O_{10})(OH)_2$	001	
Talc	$Mg_3(Si_4O_{10})(OH)_2$	001	88
Iodyrite	AgI		20

possible for specially prepared surfaces which are highly water repellant. For example, water contact angles exceeding 150° have been observed for specially prepared surfaces as shown in **Figure 3**.

Nonpolar Surfaces

It is evident that the hydrophobic surface state is established by nonpolar surfaces which are not extensively hydrated. Now the nonpolar surface criterion for hydrophobicity is well known and has been established for some time. Such characteristics of the hydrophobic surface state have been known since the mid-1950s. In some cases the hydrophobic surface state is due to the elemental composition of the surface; the surface is composed of elements of low polarity that do not hydrogen bond with water molecules. These elements include C, H, S, and large atoms of low polarizability. Examples include graphite, coal, elemental sulfur, and iodyrite. Even the surfaces of metal sulfide minerals are reported to be hydrophobic in the absence of oxygen and can be considered to be intrinsically hydrophobic. Of course, exposure to even parts per billion of oxygen can lead to oxygen fixation and subsequent complex electrochemical reactions, the surface products of which may or may not be hydrophilic depending on solution chemistry and the extent of oxidation. In general, simply the fixation of oxygen at sulfide mineral surfaces can provide sufficient surface polarity to create a hydrophilic state. Nevertheless, under anaerobic conditions the sulfide surface is expected to be hydrophobic due to its limited ability to hydrogen bond with interfacial water molecules.

In addition to the elemental composition of the surface, the crystal structure and bonding influence the polarity of mineral surfaces. In some cases, specifically surfaces that are created by breakage of weak van der Waals bonds, a nonpolar surface is created even containing elements that normally would hydrogen bond and be hydrated by interfacial water molecules. Examples include pyrophyllite, talc, and boric acid. In this way it has been established that the hydrophobic nonpolar surface state can arise from the intrinsic properties of the elements of which the surface is composed and from bonding considerations associated with the crystal structure. Finally it should be noted that hydrophobic surfaces can be charged just as hydrophilic surfaces are and that generally maximum hydrophobicity is found at the isoelectric point, or the point of zero charge, of the surface.

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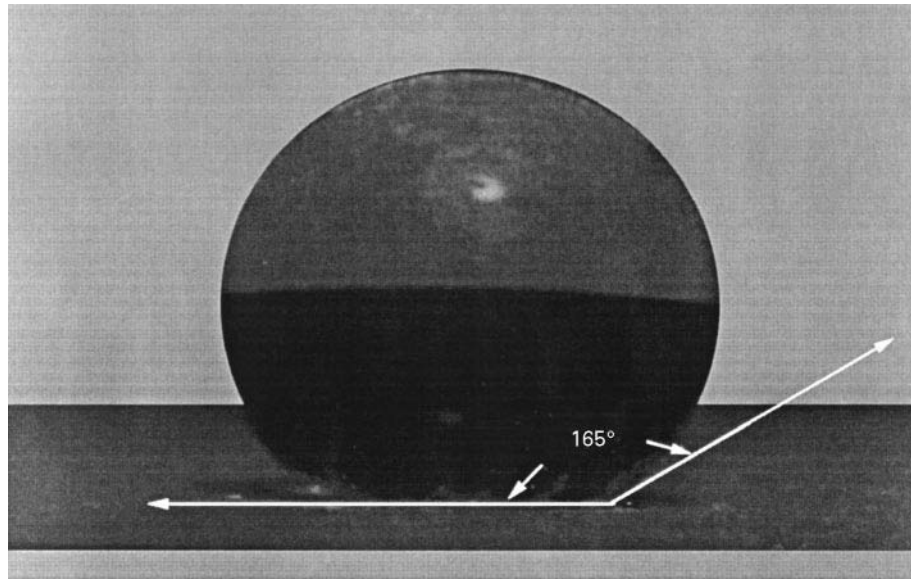

Figure 3 Water contact angle for a sessile drop of water at the surface of a newly developed water repellant material.

Water Film Stability

Of course the hydrophobic surface state must not only be described in terms of the elemental surface composition and structure but also must be described in terms of the interfacial water structure; in fact the instability of the interfacial water film accounts for bubble attachment at a hydrophobic surface. The characteristic features of interfacial water and its instability at a hydrophobic surface have not been so well described until recently. Now with the use of atomic force microscopy, surface spectroscopy, and a laser optical cavity technique, these features of interfacial water have been revealed in greater detail.

Direct force measurements during the 1980s and 1990s have revealed that attractive hydrophobic forces are usually 10 to 100 times larger than those expected from van der Waals interactions. These forces extend to distances of as much as 100–200 nm from the surface. The extent of attraction between hydrophobic surfaces is related to the degree of hydrophobicity but seems to be also independently effected by discrete features of the surface like roughness and heterogeneity.

At the same time, during the 1990s, *in situ* surface spectroscopy (sum frequency generation (SFG) and Fourier transform infrared/internal reflection spectroscopy (FTIR/IRS)) of water at hydrophobic surfaces has revealed important characteristics of interfacial water. The SFG spectral information clearly shows a distinction between water at a hydrophobic surface and water at a hydrophilic surface. Interfacial water at a hydrophobic surface is distinguished by a stronger absorption band at 3600 cm^{-1} characteristic of a dangling free OH bond. In contrast, interfacial water at a hydrophilic surface is distinguished by a diminished absorption band at 3600 cm^{-1} and a stronger signal at 3200 cm^{-1} characteristic of an ice-like structure with complete tetrahedral coordination. Based on these surface spectroscopy studies, it appears that interfacial water at a hydrophilic surface can be viewed as organized dipoles in tetrahedral coordination and oriented with respect to the polarity of the hydrophilic surface, whereas interfacial water molecules at a hydrophobic surface are not so well organized at the surface and have incomplete tetrahedral coordination with dangling free OH bonds.

It might be assumed that this *in situ* spectral data can then be used to account for film instability at a hydrophobic surface. Unfortunately, it seems that the phenomenon is not that simple. It is expected that the interfacial water structure will extend only a distance of a few molecular diameters, not more than a few nanometers or so. On the other hand, the hydrophobic attractive forces can extend to 100 nm, and even more. Thus it would seem that film instability at a hydrophobic surface involves more than just the hydrogen bonding characteristics of interfacial water.

Some researchers have attributed film instability to cavitation phenomena. The presence of nanobubbles or defects in the interfacial water region at a hydrophobic surface has been reported based on experimental results using a laser optical cavity technique. Also it should be noted that surface force measurements reveal that the range of the attractive hydrophobic force is significantly greater in gas-saturated solution then in degassed solution. It is expected that slight perturbations in the pressure field would cause these nanobubbles to coalesce and form cavities which upon further coalescence would lead to cavitation and failure of the water film at a hydrophobic surface as shown in **Figure 4**. In some cases, discontinuities during force measurements were observed which may be attributed to the phase transition (cavity formation) between approaching surfaces. Finally, recent FTIR/IRS spectroscopic evidence, indeed, shows that dissolved gas is accommodated at a hydrophobic surface but not so at a hydrophilic surface. Thus the presence of nanobubbles in the interfacial water region of a hydrophobic surface is supported by these spectroscopic results.

Summary

In summary, the hydrophobic surface state must be considered both with regard to the particle surface and with regard to the adjacent interfacial water

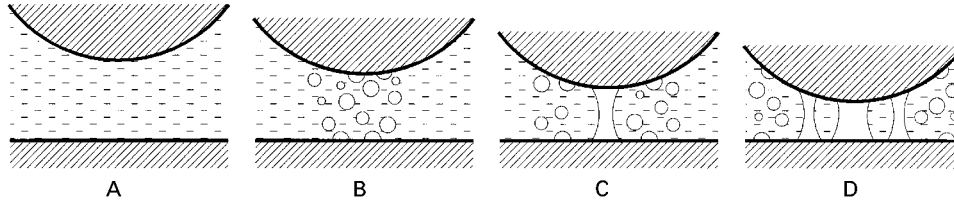

Figure 4 Schematic picture of cavitation phenomena during approach of hydrophobic sphere and hydrophobic plane in water. (A) Layers of lower medium density (adsorbed gas molecules), (B) nanobubbles formation, (C) bridging cavity formation, and (D) multiple bridging cavities, leading to film rupture and attachment.

region. The particle surface must be of low polarity which is determined by elemental composition and/or structural bonding considerations. Water film instability at a hydrophobic surface arises not only from a disrupted interfacial water structure but also from a cavitation phenomenon which involves coalescence of nanobubbles in the interfacial water region. Such is the nature of the hydrophobic surface state.

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Intensive Cells: Design

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Introduction

In conventional flotation practice, the particles to be treated are dispersed in a suspension in water. Reagents are added to make the particles to be floated hydrophobic or nonwetting. The particles which are to be left behind remain in a wettable state. Air bubbles are then introduced into the slurry or pulp in a contacting device or cell, and collide with the nonwetted particles, carrying them to the surface where they form a froth. The froth concentrate flows over a weir and out of the flotation cell, while the unwanted tailings flow out of the bottom.

The effectiveness of this type of cell lies in the ability of the bubbles rising in the liquid to collide with particles in suspension. Because the concentration or hold-up of air in the liquid is not very high – typically less than 10% by volume – the probability of a collision is correspondingly low. The low frequency of useful collisions between an individual bubble and the particles in a flotation machine can be overcome by increasing the residence time of the suspension. In this way, by using long residence times which can sometimes be as much as an hour in a